A note on chirality in NMR spectroscopy

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In a recent pair of papers, Buckingham and Buckingham and Fischer proposed methods on how "chiral blindness" may be removed in NMR.[1,2] Here, we give proofs of their derivations of the manifestation of chirality in the chemical shift and spin-spin coupling constant using simple symmetry arguments. We then relate our proofs to earlier discussions by Mead *et al.*[3] and by Sears *et al.*[4]

The effective Hamiltonian for nuclear spins may be obtained from the ground state energy of the electronic and nuclear system in which they are embedded. This energy must be time even and an overall scalar. In the presence of a static electric field $\boldsymbol{E}$, static magnetic field $\boldsymbol{B}$, and nuclear spin operator $\boldsymbol{S}$, for an isotropic system the only scalar that may be formed from these three vectors is a pseudoscalar,

$$\mathrm{PS} = \boldsymbol{S} \cdot \boldsymbol{B} \times \boldsymbol{E}, \tag{1}$$

which is time even. Hence the ground state energy may be written as

$$E_G = \sigma \boldsymbol{S} \cdot \boldsymbol{B} + \sigma_{\mathrm{chiral}} \boldsymbol{S} \cdot \boldsymbol{B} \times \boldsymbol{E}. \tag{2}$$

Under parity, E_G is unchanged; however,

$$\sigma_{\mathrm{chiral}} \rightarrow -\sigma_{\mathrm{chiral}}, \tag{3}$$

so σ_{chiral} must be a pseudoscalar. Hence, the chiral portion of the chemical shift for each enantiomer is

$$\sigma_L = \sigma_{\mathrm{chiral}} \tag{4}$$

and

$$\sigma_R = -\sigma_{\mathrm{chiral}}, \tag{5}$$

respectively.

We use identical arguments to obtain the chiral portion of the spin-spin coupling. Suppose there are two nuclear spin operators $\boldsymbol{S}_1$ and $\boldsymbol{S}_2$ and the external field $\boldsymbol{E}$. The only time-even scalar that may be formed from these three vectors is the pseudoscalar PS; given by

$$\mathrm{PS}' = \boldsymbol{E} \cdot \boldsymbol{S}_1 \times \boldsymbol{S}_2. \tag{6}$$

Hence the spin-spin coupling contribution to the ground state energy may be written as

$$E_G = J \boldsymbol{S}_1 \cdot \boldsymbol{S}_2 + J_{\mathrm{chiral}} \boldsymbol{E} \cdot \boldsymbol{S}_1 \times \boldsymbol{S}_2. \tag{7}$$

Under parity, E_G is unchanged; but

$$J_{\mathrm{chiral}} \rightarrow -J_{\mathrm{chiral}},$$

so J_{chiral} also must be a pseudoscalar. Hence, the chiral portion of the spin-spin coupling for each enantiomer will be

$$J_L = J_{\mathrm{chiral}} \tag{8}$$

and

$$J_R = -J_{\mathrm{chiral}}, \tag{9}$$

respectively.

These proofs of existence do not suggest how large the chiral quantities are.

It is of interest to relate the above proofs to the proof, which Mead *et al.* advanced, that in equilibrium static electric and magnetic fields cannot chirally discriminate.[3] They used symmetry arguments to arbitrary powers of $\boldsymbol{B}$ and $\boldsymbol{E}$. From the point of view of the above proof, their argument may be simply stated as follows: one cannot construct a time-even pseudoscalar with one time-even vector $\boldsymbol{E}$ and one time-odd pseudovector $\boldsymbol{B}$. There will always be a dangling time-odd pseudovector only removable by the presence of a third time-odd pseudovector.

In a recent paper, we simulated the creation of diastereomers by attaching helical partial charge arrays to chiral complexes.[4] Unlike the addition of a fixed external field, the attached field is considered as part of the molecule when an orientation average is performed. Hence, the ground state energy will have two labels, (L,R) for the molecule and (l,r) for the chiral potential. Thus we have, in the weak field limit,

$$E_{Ll} = E_{Rr} = (\boldsymbol{S} \cdot \boldsymbol{B})(\sigma_{\mathrm{even}} + \sigma_{\mathrm{odd}}) \tag{10}$$

and

$$E_{Lr} = E_{Rl} = (\boldsymbol{S} \cdot \boldsymbol{B})(\sigma_{\mathrm{even}} - \sigma_{\mathrm{odd}}), \tag{11}$$

"Even" and "odd" refer to the decomposition of the external field into even and odd spherical harmonics. NMR is "blind" to a full mirror image. But NMR can distinguish diastereomers.

Of course NMR, without external electric fields, without diastereomers, is not totally blind. Parity is not conserved, so there is a tiny pseudoscalar component to the shift,[5] or

$$E_L = (\boldsymbol{S} \cdot \boldsymbol{B})(\sigma + \delta), \tag{12}$$

$$E_R = (\boldsymbol{S} \cdot \boldsymbol{B})(\sigma - \delta), \tag{13}$$

where δ is the tiny manifestation of parity nonconservation.

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